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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

New Method For the Determination of Uranium (IV), Uranium (VI) and Total Uranium In Solutions Obtained During Leaching of Phosphate Ores by Hydrochloric Acid

by

L.A. GUIRGUIS and M.A. WASSEF*

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

New Method For the Determination of Uranium (IV), Uranium (VI) and Total Uranium In Solutions Obtained During Leaching of Phosphate Ores by Hydrochloric Acid

L.A. GUIRGUIS and M.A. WASSEF*

Nuclear Material Corporation, Cairo, Egypt.

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ABSTRACT

In marine phosphate of safaga, Egypt, tetravalent Uranium, U(IV) is found to be between 70 to 80 % of the total uranium. However, the phosphatic sandstone of Qatrani, Egypt, is nearly devoid of U(IV). As shown by autoradiographs, uranium is mainly concentrated in the carbonate Fluorapatite, Francolite or Collophane minerals.

The U(IV) and U(VI) content of process solution samples during phosphoric acid production are obtained. Firstly by dissolving the samples by hydrochloric acid under normal conditions. Secondary by dissolving the samples in an oxidizing atmosphere. The uranium concentration is determined by fluorimetry. The achieved results are presented and found to be in good agreement with that obtained by tri-n-octylamine extraction and polar-ography.

INTRODUCTION

Sedimentary marine phosphates contain from 0.004 to 0.02 percent uranium. Despite their low uranium content as compared to other ores, they are promising source of uranium as a by-product of the manufacture of triplesuperphosphate.

Generally, uranium modes of occurences in phosphates involves its presence as either U^{4+} (1) or $(UO_2)^{2+}$ isolated and chemically adsorbed or else structurally emplaced in the lattice (2). Uranium can also be present as an oxide impurity (3).

According to Clarke and Altschuler (4), U(IV)/U(VI) ratio in phosphate rock can be determined by dissolving the sample in cold HCl or

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* Ghemistry Dept., Univ. College for Women, Ain Shams Univ., Cairo.

H_3PO_4, and U(IV) is precipitated by cupferron with Ti(IV) as carrier. Both U(IV) and the total uranium concentration is determined fluorimetrically.

One method (5) designed for the determination of U(VI)/U(IV) ratio in a mixture of phosphoric and hydrochloric acids is by extraction with tri-n-octylamine in xylene. Uranium(VI) is re-extracted from the loaded solvent by 4N HCl. U(IV) is oxidised with ferric chloride before extraction. The concentration of uranium is determined polarography.

The method given here is based on the differential solubility of uranium versus phosphorus pentoxide This depends on the inherited chemical properties of uranium, since while its tetravalent stage is insoluble in dilute mineral acids, hexavalent uranium readily dissolves. The uranium concentration is determined by fluorimetry (6).

EXPERIMENTAL

Three samples from different localities at Egypt are examined namely, Bahari Nasser, Wassif and Qatrani phosphatic sandstone. El Shazly *et al* (7) have studied the minorology, geochemistry and origin of these ores. Table (1) shows their complete chemical analysis obtained by following the same procedure mentioned previously (8).

Table 1. Chemical Analysis of the Studied Ores.

Element %	Qatrani	Bahari Nasser	Wassif
SiO_2	69.81	18.75	12.03
P_2O_5	10.30	20.06	27.36
CaO	14.60	35.40	43.14
MgO	U.D+	4.34	1.78
Fe_2O_3	0.73	1.51	1.84
FeO	0.08	0.12	0.42
Al_2O_3	1.47	1.83	0.79
Na_2O	0.13	0.28	0.22
K_2O	0.05	0.02	0.02
SO_3	0.30	3.66	1.55
F^-	1.07	2.10	3.25
Cl^-	0.24	0.26	0.26
CO_2	1.89	9.05	6.55
Moisture content	U.D	0.23	0.58
Organic matter	0.31	1.47	0.47
Ignition loss	2.20	10.00	7.40
Total U ppm	700	45	64

* Under detection limit.

In the present study, uranium /apatite dependence has been confirmed by neuclar emulsion plates to locate the radioactive mineral and/or elements by its application to uncovered thin slices (autoradiograph). The results are represented in Figs. 1 to 3, where the α tracks correspond to either Collophane or Francolite minerals. The plates used are those of Ilford C_2, 50 μ in thickness. After careful fixation, Qatrani phosphate samples are left for one month while for those of Bahari Nasser and Wassif, an exposure time of four months has been found necessary. The plates were then developed for 25 mins. in a mixture of equal volumes of solution A (100 g K_2CO_3 + 20 g Na_2SO_3 + 1 g KBr /l) and solution B (1% of hydroquinone).

After washing with distilled water, the plates were put in a 2% solution of acetic acid (stopping bath) for 6 min. and then washed with water again. Fixing was finally performed by 35% sodium thiosulphate solution for 30–45 mins., followed by a running water wash for 30 mins. Before drying, the plates were carefully cleaned with wet cotton to remove the powder grains which might remain on the gelatinous layer. The U(IV) and U(VI) determinations of the investigated phosphate ores have been obtained through selective hydrochloric acid leaching

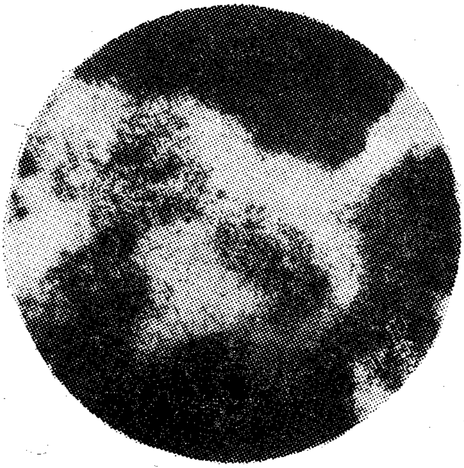


Fig. (1–A): Autoradio graph of Bahari Nasser phosphate ore showing the α tracks due to collophane. × 360 (time of exposure 120 days).

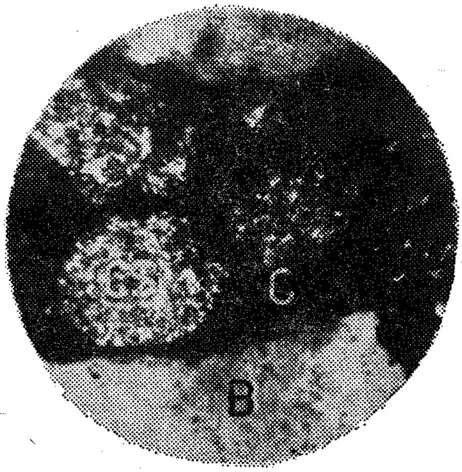


Fig. (1–B): Bahari Nasser phosphate ore showing collophane. (C) chalcedoney replacing the collophane (CS), and bone fragments (B). Radioactivity is due to collophane.

under normal and oxidizing conditions. The general procedure followed involved the following: 100 g of each ore was suspended in 250 ml distilled water in one 1 round bottom flask with three opening. A central wide opening is fitted with a glass stirrer through a water-sealed device.

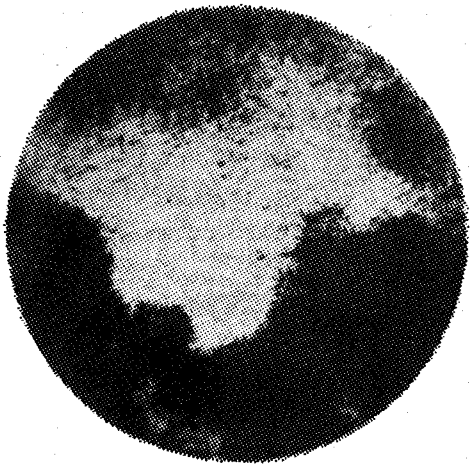


Fig. (2–A): Autoradiography of Wassif phosphate ore showing the α tracks due to collophane × 360 (time of exposure 120 days).

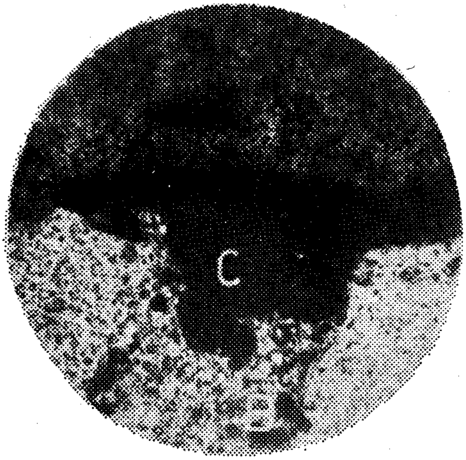


Fig. (2–B): Wassif phosphate ore showing collaphane (C) and bone fragments (B). Radioactivity due to collophane × 360.

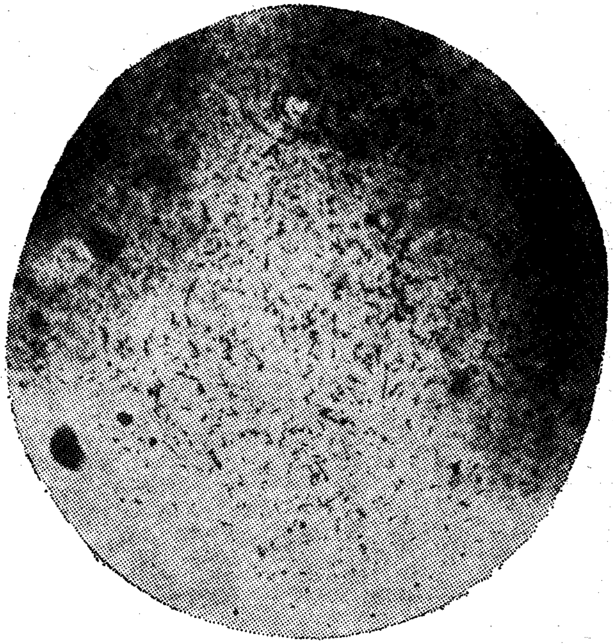


Fig. (3–A): Autoradiography of Qatrani phosphatic sandstone showing the α tracks due to francolite. × 360 (time of exposure 30 days).

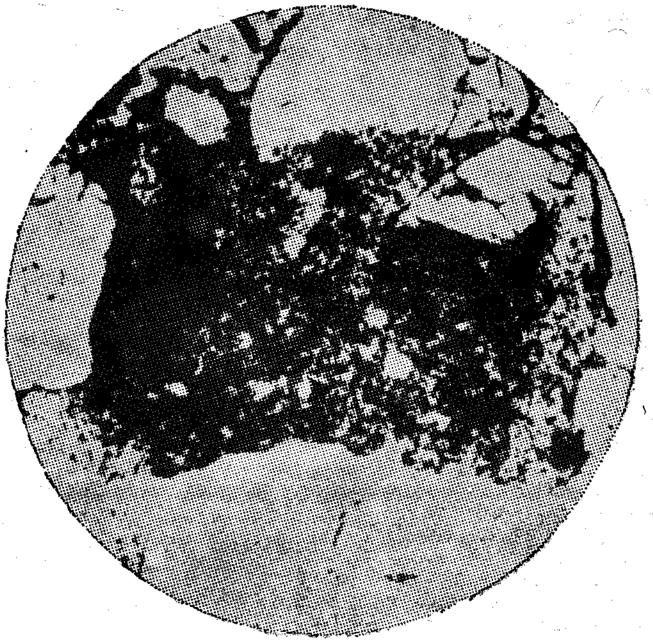


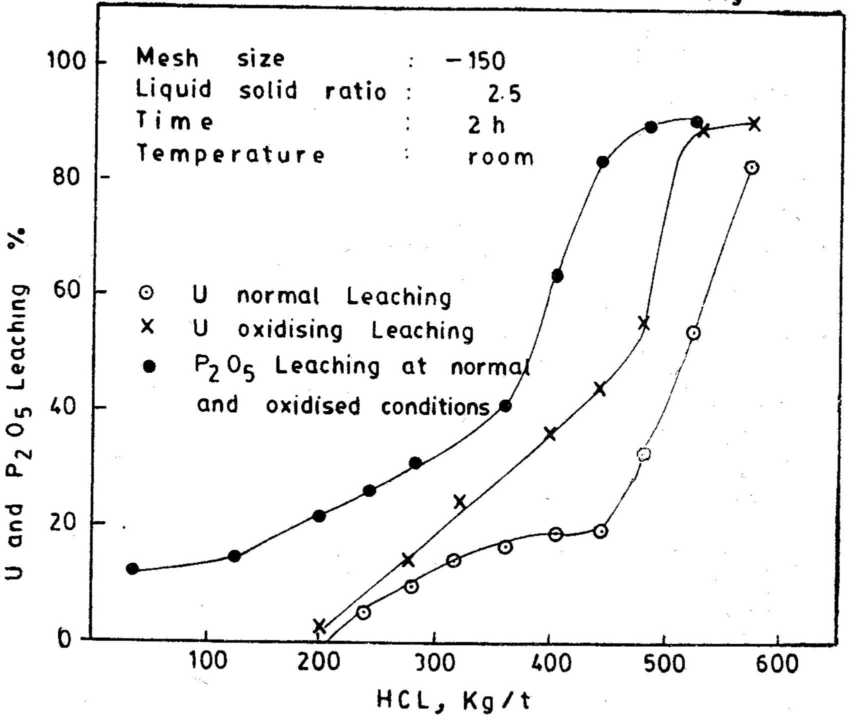
Fig. (3–B): Qatrani phosphatic sandstone showing the presence of francolite (grey) as a matrix for the Quartz (white). × 360.

To one of the side opening a graduated device is connected, through which 100 ml of 12N HCl was then added in 10 ml aliquots. The slurry was stirred for 2 h., and 10 ml aliquots of the supernatant liquid was withdrawn for analysis from the third opening. For the experiments under oxidizing conditions, 2% of manganese dioxide was used.

RESULTS

Uranium an P_2O_5 results of Bahari Nasser raw mine phosphate ore type selective leaching experiments using HCl in amounts up to 640 kg/t are plotted in Fig. 4.

Fig (4)



HCL agitation Leaching of Bahari Nasser phosphate ore under normal, and oxidising conditions.

U and P_2O_5 Leaching as functions of acid quantity.

It is clearly evident from the achieved results that uranium leaching efficiency is greatly influenced by the oxidation state of the medium. Thus, under normal conditions 19% of the uranium is only dissolved at relatively small acid concentration amounting to less than 400 kg/t. By exceeding the HCl acid amount beyond this limit, uranium dissolution increases rapidly On the other hand, under oxidizing conditions using 2% MnO_2 nearlty all the uranium is dissolved and all the time it is parrallel to that of P_2O_5 leaching data and no flatness in the leaching curve is observed.

At relatively small acid concentration up to 200 kg HCl/t ore, P_2O_5 dissolution is faster than that of uranium, probably due to the first dissolution of acid consuming material (gange minerals). At high acid concentration the two curves of P_2O_5 and U at oxidizing condition are nearly parrallel, indicating that as soon as an amount of P_2O_5 is dissolved its contained uranium dissolved as well.

The obtained results of uranium and P_2O_5 on Wassif phosphate ore selective leaching experiments using HCl in amounts up to 720 kg/t are given in Fig.5. These also show that the uranium leaching efficiency is influenced by the oxidation state of the medium. Thus, under normal condition, only 29% of uranium is dissolved at HCl aciduation rates less than about 480 Kg/t, after which the uranium starts again to dissolve steadily.

On the other hand, the P_2O_5 leaching efficiency is completely independent of the oxidation state of the medium and increases with the acid concentration up to about 480 kg/t ore.

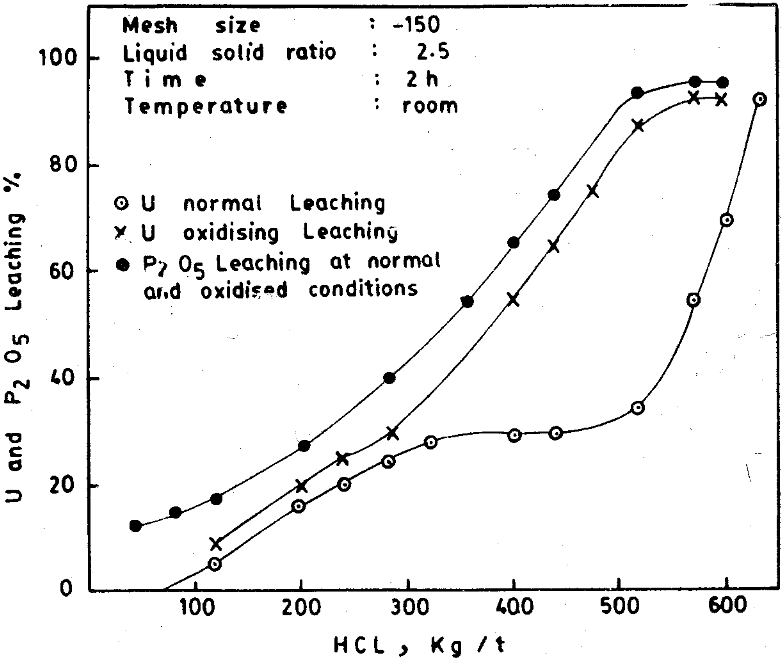
Similar to Bahari Nasser phosphate under oxidizing conditions all the uranium is dissolved and all the time it is parallel to that of P_2O_5 leaching percent.

The same leaching experiments have been performed upon phosphatic sandstone of Qatrani. The introducing peculiarity of the achieved uranium leaching efficiencies is that almost identical results have been obtained under either the normal oxidizing leaching conditions. Complete leaching of both uranium and P_2O_5 is obtained at 160 kg HCl/t ore.

DISCUSSION

Conditions at low acid concentrations bring about solubilization of the uranium present in the hexavalent state as the phosphate is leached. Increasing the acidulation rates after wards does not, however, increase uranium leaching (Flatness) although phosphate is being leached and that this behaviour continues till certain acidulation limit at which the phosphate is completely leached. It is only beyond the latter that uranium starsts to redissolve (Figs. 5 and 6).

Fig. (5)

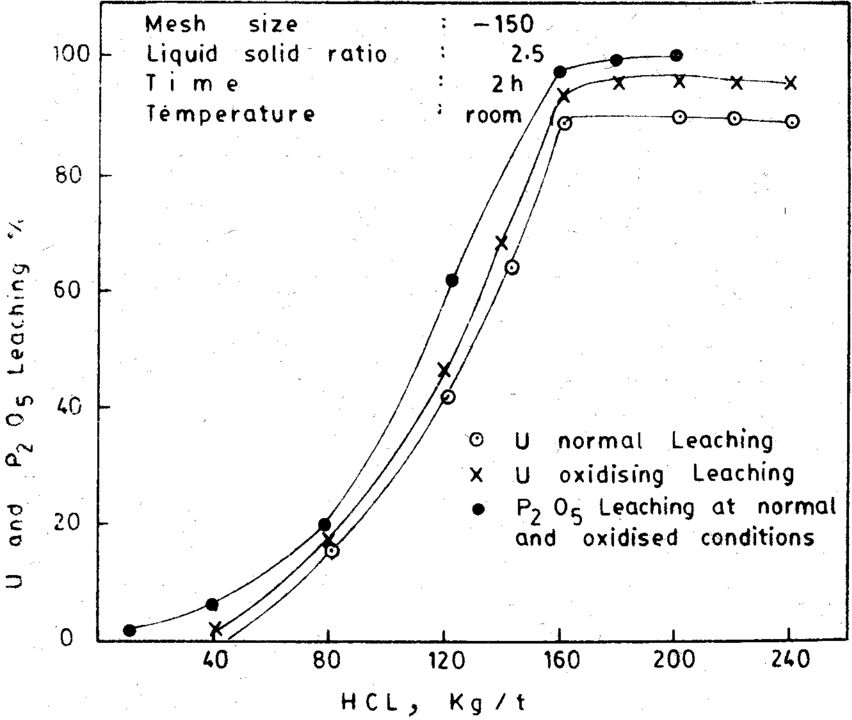


HCL agitation Leaching of Wassif row phosphate ore under normal and oxidising conditions.

U and P_2O_5 Leached as functions of acid quantity.

This behaviour can actually be accounted for by the fact that at low acidulation rates the dissolved phosphate reports in solution as monocalcium phosphate. The latter having only weak acid properties (pH 2) could leach the hexavalent uranium and is, however, unable to dissolve the tetravalent uranium which is thus kept behind in the residue. Increasing the acidulation rate equivalent to complete phosphate leaching and at which all the phophate is reported in solution as monocal-

(6)
Fig.



HCL agitation Leaching of Qatrani phosphatic sandstone under, normal and oxidising conditions. U and P_2O_5 Leached as functions of acid quantity.

cium phosphate, uranium(IV), starts to dissIove. This is due to the fact that monocalciom phosphate woult starts to be converted to phosphoric acid which is able to dissolve the tetravalent uranium by vertue of its complexing nature.

According to Altschuler *et al* (4) both U(IV) and Fe(III) form stable compounds with the fluoride and orthophosphate.

The fact that U(IV) forms stable ortho-phosphate complexes in phosphoric acid solution to an extent that limits air oxidation of U(IV) has been proved (9). It is interesting in this regard to refer to the acidulation of Qatrani phosphatic sandstone under normal conditions which did not yield any plateau in the curves of uranium leaching. In otherwards, uranium leaching efficiency is completely parallel to that of P_2O_5 even before H_3PO_4 acid is produced. This has been interpreted that nearly all the uranium present in the latter ore material exists primarily in the easily soluble hexavalent form (UO_2HPO_4) uranyl hydrogen phos sphate as mentioned by El Shazly *et al* (10). On the other hand, leaching marine phosphate ores (Bahari Nasser and Wassif) under oxidizing conditions did not show any plateau in the uranium leaching effiency, i.e. uranium leaching efficiency is all the time proportional to that of phosphate even before production of phosphoric acid. At any phosphate dissolution rate, an equivalent amount of uranium (IV) is liberated and is at once oxidized and becomes therefore amenable for leaching in the weakly acidic solution of the monocalcium phosphate. In Qatrani phosphatic sandstone, this behaviour is attained without the need of incorporating any oxidizing material in the leaching medium.

Conclusion: Both U(IV) and U(VI) could be determined in phosphate ores through differential solubility of uranium versus phosphorus pentoxide. The obtained results are in good agreement with that using tri-n-octylamine extraction and polarography (5) as shown from Table 2.

Table 2. Determination of Uranium (IV), Uranium (VI) in the studied ores dissolution liquors.

Phosphate ore	This work Relative mean deviation 4%		Polarography$^+$ Relative mean deviation 2%	
	% U(IV)	% U(VI)	% U(IV)	% U(VI)
Bahari Nasser	81	19	80	20
Wassif	71	29	69	31
Qatrani	97	3	98	2

* Polarography results are obtained following the same experimental procedure of Hodara and Balouka (5).

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